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(54) CATALYST FOR PURIFYING EXHAUST GAS

(57)Abstract:

PURPOSE: To obtain a ternary catalyst for an internal combustion engine high in durability.

CONSTITUTION: A catalyst carrier is coated with a mixture consisting of catalytically active components prepared by supporting platinum and/or palladium on cerium oxide stabilized by rare earth metal (excepting zirconium and cerium) and zirconium and refractory inorg. oxide based on activated alumina and, thereafter, rhodium and/or rhodium and a platinum group metal are further supported on the carrier to obtain the objective catalyst for purifying exhaust gas. Since platinum and/or palladium are preliminarily supported on stabilized cerium oxide, the sintering of platinum and palladium is suppressed and catalytic activity can be kept long.

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JAPANESE

[JP,07-299360,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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 CLAIMS

[Claim(s)]

[Claim 1] The catalyst for exhaust gas clarification characterized by coming to support a rhodium and/or a rhodium, and a platinum metal further after making catalyst support cover with a zirconium, or the rare earth metal and zirconium except a cerium the mixture which turns into cerium oxide by which heat stabilization was carried out from the catalytic activity component which supported platinum and/or palladium, and the fireproof inorganic oxide which made the activated alumina the subject.

[Claim 2] The catalyst for exhaust gas clarification according to claim 1 currently supported by the cerium oxide with which heat stabilization of at least 30% of the weight or more of the total amount of the platinum currently supported and/or palladium was carried out.

[Claim 3] The catalyst for exhaust gas clarification according to claim 1 whose amount of support of a rhodium the amount of support of platinum and/or palladium is 0.1–5.0g/l. per unit capacity of a catalyst, and is 0.01–1.0g/l.

[Claim 4] The catalyst for exhaust gas clarification according to claim 1 whose amount of support of a rhodium the amount of support of platinum and/or palladium is 0.3–3.0g/l. per unit capacity of a catalyst, and is 0.05–0.5g/l.

[Claim 5] 50% of the weight or more of a rhodium is the catalyst for exhaust gas clarification according to claim 1 currently supported within 40 micrometers from the front face of the layer which consists of a fireproof inorganic oxide covered by catalyst support.

[Claim 6] The catalyst for exhaust gas clarification according to claim 1 10–200g, and whose fireproof inorganic oxide the cerium oxide by which heat stabilization was carried out is 80–300g per 1l. of catalyst support.

[Claim 7] It is the catalyst for exhaust gas clarification according to claim 1 whose specific surface area the mean particle diameter of the cerium oxide by which heat stabilization was carried out is 10 micrometers or less, and is more than 20m² / g.

[Claim 8] The cerium oxide by which heat stabilization was carried out is a catalyst for exhaust gas clarification according to claim 1 in which it is the mixture of cerium oxide, a zirconic acid ghost, and the rare earth oxide except cerium oxide, and at least the part exists as a multiple oxide or the solid solution.

[Claim 9] The multiple oxide or the solid solution of cerium oxide, a zirconic acid ghost, and rare earth oxide is a catalyst for exhaust gas clarification according to claim 5 constituted so that a zirconium may be served as to 0.05 to 0.35 by the remainder and the sum total of zero to 0.30, a zirconium, and a rare earth metal may serve as [a rare earth metal] a cerium respectively at an atomic rate 0.05–0.55.

[Claim 10] A fireproof inorganic oxide is a catalyst for exhaust gas clarification according to claim 1 which are an activated alumina, the activated alumina by which heat stabilization was carried out, the oxide of a rare earth metal, and the oxide of alkaline earth metal.

[Claim 11] An activated alumina is a catalyst for exhaust gas clarification according to claim 1 whose mean particle diameter is 10 micrometers or less and whose specific surface area it is kinds of gamma-alumina, delta-alumina, and theta alumina, or such mixture, and is more than 50m² / g.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the catalyst for exhaust gas clarification which removes simultaneously the carbon monoxide (CO), the hydrocarbon (HC), and nitrogen oxides (NOx) which are the injurious ingredients contained in the exhaust gas from internal combustion engines, such as an automobile, about the catalyst for exhaust gas clarification.

[0002]

[Description of the Prior Art] Conventionally, in the three way component catalyst which removes simultaneously the carbon monoxide, the hydrocarbon, and nitrogen oxides which are the injurious ingredients in the exhaust gas discharged by the internal combustion engine, the cerium oxide which has oxygen storage effect mainly for platinum group metals, such as platinum and a rhodium, and the improvement in low-temperature activity is used.

[0003] Such a conventional catalyst for exhaust gas clarification performs coating by the slurry of an activated alumina, sinks into a cerium solution after that, and is performing impregnation support to integral-construction mold monolith support using platinum-group-metals content solutions, such as platinum and a rhodium, after that further. there is an inclination for the installation of these catalysts to be carried out directly under [more near an engine] a manifold recently — moreover, the elevated-temperature thermal resistance of a catalyst has been more greatly required by lifting of the exhaust gas temperature at the time of high-speed operation etc.

[0004] However, the catalyst containing conventional platinum group metals and cerium oxide tends to deteriorate in an elevated temperature. In order to raise the elevated-temperature thermal resistance of a catalyst for this reason, the oxide of a rare earth metal or alkaline earth metal is added. Moreover, if a long duration activity is carried out at an elevated temperature, the so-called sintering which a platinum particle condenses and causes grain growth will occur, and the clarification engine performance will deteriorate remarkably. The catalyst which supported platinum on cerium oxide for the sintering control of platinum to JP,5-20435,Y is indicated.

[0005]

[Problem(s) to be Solved by the Invention] However, although the above-mentioned conventional three way component catalyst showed the good 3 way activity for purifying three components of CO, HC, and NOx in the first stage, it was not necessarily able to say that it was enough in endurance or thermal resistance in the large part of fluctuation of an elevated temperature [like / directly under a manifold], and a gas ambient atmosphere component.

[0006] Therefore, in the catalyst which uses platinum and/or palladium, and a rhodium as a catalyst component, simultaneously, this invention is stabilized, purifies three components of CO, HC, and NOx over a long period of time, from the first stage, and is to offer the catalyst which can maintain the endurance in an elevated temperature.

[0007]

[Means for Solving the Problem] The catalytic activity component which supported platinum and/or palladium with the zirconium, or the rare earth metal and zirconium except a cerium to the cerium oxide by which heat stabilization was carried out as a result of inquiring wholeheartedly, in order that this invention person may solve this technical problem, After making catalyst support cover the mixture which consists of a fireproof inorganic oxide which made the activated alumina the subject, Furthermore, it comes to complete a header and this invention for the catalyst engine performance improving compared with the catalyst in which the catalyst for exhaust gas clarification which comes to support a rhodium and/or a rhodium, and a platinum metal contains platinum and/or conventional palladium, and a conventional rhodium.

[0008] As for the amount of support of the platinum and/or palladium which are supported by a catalytic activity component and the fireproof inorganic oxide, it is desirable that it is 0.1-5.0g/l. per unit capacity of a catalyst. When the amount of support of platinum and/or palladium is less than 0.1g/l. per unit capacity, there is a possibility that sufficient clarification engine performance may not be obtained. Moreover, even if the amount of support of platinum and/or palladium exceeds 1. in 5.0g /per unit capacity conversely, only the effectiveness of balancing the amount of support is not acquired. Especially, the case where the amount of support of platinum and/or palladium is 0.3-3.0g/l. per unit capacity is more more desirable than the field of catalytic activity and cost.

[0009] Moreover, it is desirable that 30% of the weight or more of the total amount of support of the platinum supported by catalyst support and/or palladium is supported by the heat stabilization cerium oxide. When the amount of support of platinum and/or palladium is less than 30%, since the sintering control at the time of an elevated temperature is not enough, it is not desirable. As for the amount of support of the rhodium supported by catalyst ****, it is desirable that it is 0.01-1.0g/l. per unit volume of a catalyst. It has a possibility that sufficient catalytic activity may not be acquired, when the amount of support of a rhodium is less than 0.01g/l. per unit volume. Moreover, even if the amount of support of a rhodium exceeds 1. in 1.0g /per unit volume conversely, only the effectiveness of balancing the amount of support is not acquired. Especially when the amount of support of a rhodium is 0.05-0.5g/l. per unit volume, it is more desirable in respect of catalytic activity and cost.

[0010] As a fireproof inorganic oxide, the oxide of alkaline earth metal, such as an oxide of rare earth metals, such as an activated

alumina by which heat stabilization was carried out with an activated alumina, silicon, and/or those oxides, and a lanthanum, magnesium, and barium, is desirable. These fireproof inorganic oxides have a desirable thing with a large specific surface area with a small particle size. In the case of an activated alumina, more than $50\text{m}^2 / \text{g}$ of mean particle diameter are [10 micrometers or less and specific surface area] good.

[0011] As for a fireproof inorganic oxide, specifically, what makes an activated alumina a subject is good. As for a fireproof inorganic oxide, what contains more than a kind of the oxide of a rare earth metal or a compound, the oxide of alkaline earth metal, or a compound in an activated alumina is good more preferably. Moreover, as for an activated alumina, what consists of kinds of gamma-alumina, delta-alumina, and theta alumina or such mixture, and contains a kind of silicon, a rare earth metal, and alkaline earth metal or its compound still more preferably for heat stabilization is good. [0012] Heat stabilization of the cerium oxide by which heat stabilization was carried out is carried out by the zirconium, or the rare earth metal and zirconium except a cerium. This cerium oxide (henceforth a heat stabilization cerium oxide) by which heat stabilization was carried out can be adjusted by the following approaches. However, a heat stabilization cerium oxide is not limited to especially the adjustment approach shown here. The approach of supporting a water-soluble zirconium salt and/or the rare earth metal salt except a cerium to commercial cerium oxide as the adjustment approach of this heat stabilization cerium oxide, the cerium salt melted in water, a zirconium salt, and/or the rare earth metal salt except a cerium can be mixed, and the approach of supporting to a fireproof inorganic oxide etc. can be raised after desiccation after mixing the rare earth metal except the approach of calcinating, a water-soluble cerium salt, a zirconium salt, and/or a cerium. In addition, 500 degrees C of baking are made by heating for about 5 hours for example, in air. By any approach, especially each salt of the rare earth metal except the cerium, zirconium, and cerium to be used is not limited, but can use a commercial nitrate, acetate, a sulfate, a chloride, etc.

[0013] The heat stabilization cerium oxide adjusted by said adjustment approach is the mixture of cerium oxide, a zirconic acid ghost, and the rare earth oxide except cerium oxide, and at least the part exists as a multiple oxide or the solid solution. When the whole is made into 100 atoms %, as for the rate of the atom of rare earth elements other than the cerium atom which constitutes heat stabilization cerium oxide, a zirconium atom, and a cerium atom, it is desirable that the atom of rare earth elements other than five to 35 atom % and a cerium atom serves as zero to 30 atom %, and the remainder serves as [a zirconium atom] a cerium atom.

[0014] Even if it calcinates in air the heat stabilization cerium oxide adjusted by the above-mentioned approach at 900 degrees C for 5 hours, specific surface area is more than $20\text{m}^2 / \text{g}$. In addition, if commercial cerium oxide is calcinated on these conditions, specific surface area will deteriorate in below $10\text{m}^2 / \text{g}$. As for each component mixed, it is desirable like the above that 10–200g, and a fireproof inorganic oxide are blended per 1l. of catalysts and for a heat stabilization cerium oxide at a rate (80–300g).

[0015] Although catalyst **** which had the mixture of a catalytic activity component and a fireproof inorganic oxide covered makes a catalyst metal support further, they are platinum metals, such as the platinum and/or palladium which were already supported by heat stabilization cerium oxide as the catalyst metal, and a rhodium, and other noble metals, and it is desirable one sort or to use two or more sorts and to support.

[0016]

[Function and Effect of the Invention] Since platinum and/or palladium were supported on the heat stabilization cerium oxide, this invention was able to control sintering which was not able to be solved conventionally. Therefore, it is an elevated temperature [like / directly under a manifold], and endurance and thermal resistance have been greatly improved also in the large location of fluctuation of a gas ambient atmosphere.

[0017] Moreover, compared with the platinum and/or palladium on the activated alumina in the conventional approach, the rate of clarification of palladium [the platinum on heat stabilization cerium oxide and/or] of CO and a NOx component improved. Moreover, as compared with the platinum and palladium on the cerium oxide by which heat stabilization is not carried out, endurance of palladium [the platinum and palladium] on the cerium oxide in which this invention carried out heat stabilization is improving remarkably. Moreover, clarification of CO and NOx which excelled [oxidization / in which this invention of this invention carried out heat stabilization / cerium] in a small amount of platinum and palladium more compared with what was mixed in the cerium salt and oxidized platinum and palladium was completed.

[0018]

[Example] Hereafter, an example explains concretely.

(Example 1) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of $120\text{m}^2 / \text{g}$ were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0019] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 2 % of the weight. Next, the coat of the slurry which becomes the monolith support with 400 cels / in², a diameter [of 80mm], and a die length of 95mm made from cordierite from the multiple oxide powder of a platinum content zirconium cerium, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and platinum, the cerium, the zirconium, and the activated-alumina content layer were formed in the monolith support made from cordierite.

[0020] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 1 was acquired. A catalyst presentation is shown in a table 1. Moreover, the blending ratio of coal of platinum, a cerium, and a rhodium was investigated for the enveloping layer cross section of this catalyst 1 by EPMA (electron probe microanalysis). Consequently, the rhodium existed in the range of 40 micrometers from the front face of an enveloping layer. Moreover, it became clear that platinum and a cerium have the presentation to which the peak etc. was similar. It turns out that platinum and a cerium approach mutually and exist from this.

[0021] (Example 2) The catalyst 1 was acquired like the example 1 except having changed the mole ratio of a cerium/zirconium into

19/1, and having changed gamma-alumina powder into the gamma-alumina powder containing La of 3 atom %. A catalyst presentation is shown in a table 1.

(Example 3) The catalyst 1 was acquired like the example 1 except having changed the mole ratio of a cerium/zirconium into 2/1, and having changed gamma-alumina powder into the gamma-alumina powder containing Ba of 3 atom %. A catalyst presentation is shown in a table 1.

[0022] (Example 4) 2.0% of the weight of the platinum content in the platinum content zirconium cerium multiple oxide of an example 1 was carried out to 1.0% of the weight, and the enveloping layer which becomes monolith support from a platinum content zirconium cerium multiple oxide and an activated alumina like an example 1 was formed.

[0023] Furthermore, monolith support with this enveloping layer was dried after being immersed in a dinitrodiamine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 4 was acquired. A catalyst presentation is shown in a table 1.

(Example 5) 2.0% of the weight of the platinum content in the platinum content zirconium cerium multiple oxide of an example 1 was carried out to 0.6% of the weight, and the enveloping layer which becomes monolith support from a platinum content zirconium cerium multiple oxide and an activated alumina like an example 1 was formed.

[0024] Furthermore, monolith support with this enveloping layer was dried after being immersed in a dinitrodiamine platinum solution, it was further immersed in the nitric-acid rhodium solution after that, the rhodium was supported, and the catalyst 5 was acquired. A catalyst presentation is shown in a table 1.

(Example 6) By 5 micrometers of mean diameters, the cerium oxide, oxy-zirconium-nitrate solution, and nitric-acid yttrium solution of specific surface area of $120\text{m}^2/\text{g}$ were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out with the zirconium and the yttrium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out with this zirconium and yttrium was 5/1/0.2 in the mole ratio of a cerium / zirconium / yttrium.

[0025] Next, the dinitrodiamine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out with the above-mentioned zirconium and the yttrium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium yttrium cerium oxide was obtained. The platinum content in this platinum content zirconium yttrium cerium multiple oxide was 2 % of the weight.

[0026] Next, the coat of the slurry which becomes the monolith support with 400 cels / in², a diameter [of 80mm], and a die length of 95mm made from cordierite from the multiple oxide powder of a platinum content zirconium yttrium cerium, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, an yttrium, and an activated alumina in monolith support was formed.

[0027] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 6 was acquired. A catalyst presentation is shown in a table 1.

(Example 7) By 5 micrometers of mean diameters, the cerium oxide, oxy-zirconium-nitrate solution, and nitric-acid ytterbium solution of specific surface area of $120\text{m}^2/\text{g}$ were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium and the ytterbium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium and ytterbium was 5/1/0.2 in the mole ratio of a cerium / zirconium / ytterbium.

[0028] Next, the dinitrodiamine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the zirconium and the ytterbium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium ytterbium cerium oxide was obtained. The platinum content in this platinum content zirconium ytterbium cerium multiple oxide was 2 % of the weight.

[0029] Next, the coat of the slurry which becomes the monolith support with 400 cels / in², a diameter [of 80mm], and a die length of 95mm made from cordierite from the multiple oxide powder of a platinum content zirconium ytterbium cerium, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, an ytterbium, and an activated alumina in monolith support was formed.

[0030] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and the catalyst 7 was acquired. A catalyst presentation is shown in a table 1.

(Example 1 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from the multiple oxide powder, the gamma-alumina powder, hydrated alumina, and pure water of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium-zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiamine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst A was acquired. A catalyst presentation is shown in a table 1. The blending ratio of coal of platinum and a rhodium was investigated for the enveloping layer cross section of this catalyst A by EPMA. Consequently, it was distributed over the range of 100 micrometers from the front face of an enveloping layer, and the rhodium was distributed over the range of 40 micrometers by platinum from the front face of an enveloping layer.

[0031] (Example 2 of a comparison) 2.0% of the weight of the platinum content in the platinum content zirconium cerium multiple oxide of an example 1 was carried out to 0.4% of the weight, and the layer which becomes the monolith support made from cordierite from platinum, a cerium, a zirconium, and an activated alumina like an example 1 was formed.

[0032] Furthermore, this monolith support was dried after being immersed in a dinitrodiamine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst B was acquired. A catalyst presentation is shown in a table 1.

(Example 3 of a comparison) The dinitrodiammine platinum solution was added and calcinated [dried and] to activated-alumina powder, and the platinum content activated alumina was obtained. The platinum content in this platinum content activated alumina was 2.0 % of the weight.

[0033] Next, the coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from a platinum content activated alumina, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, and an activated alumina in the monolith support made from cordierite was formed.

[0034] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst C was acquired. A catalyst presentation is shown in a table 1.

(Example 4 of a comparison) The dinitrodiammine platinum solution was added and calcinated [dried and] to cerium oxide powder, and platinum content cerium oxide was obtained. The platinum content in this platinum content cerium oxide was 2.0 % of the weight.

[0035] Next, the coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from platinum content cerium oxide, the multiple oxide powder of a cerium zirconium, gamma-alumina powder, hydrated alumina, and pure water was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the layer which contains platinum, a cerium, a zirconium, and an activated alumina in the monolith support made from cordierite was formed.

[0036] Furthermore, this monolith support was immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst D was acquired. It is shown in the catalyst presentation table 1.

[0037]

[A table 1]

触媒	アルミナの コート量 (g/リッ トル)	P t / P d 担持量 (g/リトル) [] は熱 安定化Ce酸化物に付 着させたPtの割合	R h 担持量 (g/リッ トル)	C e - Z r - 希土類金属 酸化物量(g/ リットル) [] はC e / Z r / 希 土類金属の原子 (数) 比
1	1 5 0	1.0/- [1 0 0 %]	0. 2	7 4 [5 / 1 / -]
2	1 5 0	1.0/- [1 0 0 %]	0. 2	7 6 [19 / 1 / -]
3	1 5 0	1.0/- [1 0 0 %]	0. 2	7 0 [2 / 1 / -]
4	1 5 0	1.0/- [5 0 %]	0. 2	7 4 [5 / 1 / -]
5	1 5 0	1.0/- [3 0 %]	0. 2	7 4 [5 / 1 / -]
6	1 5 0	1.0/- [1 0 0 %]	0. 2	7 3 [5 / 1 / 0. 2] イットリウム
7	1 5 0	1.0/- [1 0 0 %]	0. 2	7 4 [5 / 1 / 0. 2] イットリウム
A	1 5 0	1.0/- [0 %]	0. 2	7 4 [5 / 1 / -]
B	1 5 0	1.0/- [2 0 %]	0. 2	7 4 [5 / 1 / -]
C	1 5 0	1.0/- [1 0 0 %] アルミナ上	0. 2	7 4 [5 / 1 / -]
D	1 5 0	1.0/- [1 0 0 %] セリア上	0. 2	7 7 [6 / - / -]

(Example 8) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which

heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0038] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 0.6 % of the weight. Next, the catalyst 8 was acquired like the example 1. A catalyst presentation is shown in a table 2.

[0039] (Example 5 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from gamma-alumina powder, hydrated alumina, and pure water about the multiple oxide powder of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst E was acquired. It is shown in the catalyst presentation table 2.

[0040] (Example 9) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0041] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 5 % of the weight. Next, the catalyst 9 was acquired like the example 1. A catalyst presentation is shown in a table 2.

[0042] (Example 6 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from gamma-alumina powder, hydrated alumina, and pure water about the multiple oxide powder of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst F was acquired. A catalyst presentation is shown in a table 2.

[0043] (Example 10) By 5 micrometers of mean diameters, the cerium oxide and the oxy-zirconium-nitrate solution of specific surface area of 120m² / g were mixed, and the cerium multiple oxide powder by which calcinated at the temperature of 500 degrees C for 1 hour, and heat stabilization was carried out by the zirconium was obtained after desiccation. The presentation of a cerium multiple oxide by which heat stabilization was carried out by this zirconium was 5/1 in the mole ratio of a cerium/zirconium.

[0044] Next, the dinitrodiammine platinum solution was added to the cerium multiple oxide powder by which heat stabilization was carried out by the above-mentioned zirconium, after desiccation, it calcinated at the temperature of 500 degrees C for 1 hour, and the platinum content zirconium cerium multiple oxide was obtained. The platinum content in this platinum content zirconium cerium multiple oxide was 10.0 % of the weight. Next, the catalyst 10 was acquired like the example 1. A catalyst presentation is shown in a table 2.

[0045] (Example 7 of a comparison) The coat of the slurry which becomes the same monolith support made from cordierite as an example 1 from gamma-alumina powder, hydrated alumina, and pure water about the multiple oxide powder of a cerium zirconium was carried out, it calcinated at the temperature of 500 degrees C after desiccation for 1 hour, and the alumina layer containing a cerium zirconium was formed on the monolith support made from cordierite. Thus, the obtained monolith support was dried after being immersed in a dinitrodiammine platinum solution, it was further immersed in the nitric-acid rhodium solution, the rhodium was supported, and Catalyst G was acquired. A catalyst presentation is shown in a table 2.

[0046]

[A table 2]

触媒	アルミナの コート量 (g/リットル)	Pt/Pd担持量 (g/リットル)〔 〕は予 めCeに付着させたPt の割合	Rh 担持量 (g/リットル)	Ce-Zr-希土類金属 量 (g/リットル)〔 〕はCe/Zr/希土類 金属の原子(数)比
8	150	0.3/-〔100%〕	0.1	74〔5/1/-〕
E	150	0.3/-〔 0%〕	0.1	74〔5/1/-〕
9	150	0.5/-〔100%〕	0.12	74〔5/1/-〕
F	150	0.5/-〔 0%〕	0.12	74〔5/1/-〕
10	150	0.5/0.5 100%	0.2	74〔5/1/-〕
G	150	0.5/0.5 0%〕	0.2	74〔5/1/-〕

(Example 11) The catalyst 11 was acquired like the example 1 except having changed gamma-alumina fine particles into the gamma-alumina powder containing Ba of pentatomic % instead of the dinitrodiammine platinum solution used in the example 1 using the dinitrodiammine platinum solution and the palladium nitrate solution. A catalyst presentation is shown in a table 3.

[0047] (Example 8 of a comparison) Catalyst H was acquired like the example 1 of a comparison except having used the palladium nitrate solution instead of the dinitrodiammine platinum solution used in the example 1 of a comparison. It is shown in the catalyst presentation table 3.

(Example 12) The palladium nitrate solution was used instead of the dinitrodiammine platinum solution used in the example 1, and the catalyst 12 was acquired like the example 1 using the gamma-alumina containing La of 3 atom % except having added 0.2 mols /of carbonic acid Ba. by Ba conversion per unit catalyst capacity further. A catalyst presentation is shown in a table 3.

[0048] (Example 9 of a comparison) Catalyst J was acquired like the example 1 except having used the palladium nitrate solution instead of the dinitrodiammine platinum solution used in the example 1. It is shown in the catalyst presentation table 3.

[0049]

[A table 3]

触媒	アルミナの コート量 (g/リッ トル)	P t / P d 担持量 (g/リットル) [] は予 めCeに付着させたPt の割合	R h 担持量 (g/リッ トル)	C e - Z r - 希土類金属 量 (g/リットル) [] はC e / Z r / 希土類 金属の原子 (数) 比
1 1	1 5 0	0.5/0.5 1 0 0 %]	0. 2	7 4 [5/1/-]
H	1 5 0	0.5/0.5 0 %]	0. 2	7 4 [5/1/-]
1 2	1 5 0	-/1.0 [1 0 0 %]	0. 2	7 4 [5/1/-]
J	1 5 0	-/1.0 [0 %]	0. 2	7 4 [5/1/-]

(Example 1 of a trial) The exhaust gas temperature of 800 degrees C of average engine-speed 3500rpm and a catalyst inlet port and the exhaust gas temperature of 1050 degrees C of a catalyst center section performed the durability test of 50 hours on the aging conditions which show the catalyst acquired in the example 1 - the example 11 and the example 1 of a comparison - the example 9 of a comparison in installation and drawing 1 at a gasoline engine with a displacement of 4000 cc.

[0050] Aging conditions are the cycles which make 1 cycle 60 seconds as shown in drawing 1, for 40 seconds begun in 1 cycle, when it controls by theoretical-air-fuel-ratio A/F=14.6 and passes over the 40th second, it increases, a fuel is set to A/F=12-13, and the condition is continued for 16 seconds (from the 40th second of 1 cycle to the 56th second). It returns to after that theoretical-air-fuel-ratio A/F=14.6, and engine control is carried out. On the other hand, installation of secondary air does not introduce secondary air as "close" from the start of 1 cycle to the 44th second, but introduces secondary air into the 44th second, and is made "open", and control continued as it is till 60 seconds is carried out. The temperature of a catalyst center section rises from the 44th second of 1 cycle, and it amounts to 1050 degrees C, and becomes the durability test to which temperature descends from 1050 degrees C under hyperoxia from the 55th second.

[0051] Each catalyst which performed the above mentioned durability test evaluated installation and the catalyst engine performance to the gasoline engine with a displacement of 660 cc next. An engine speed is controlled by 3000rpm and theoretical-air-fuel-ratio A/F=14.6, the temperature of a catalyst inlet port is changed, and assessment conditions are HC, CO, and NOx. Clarification temperature was searched for 50%. An assessment result is shown in a table 4 - a table 6.

[0052]

[A table 4]

触媒	担持量 (g/l)		耐久後 50% 浄化温度 (℃)		
	P t	R h	H C	C O	N O _x
1	1. 0	0. 2	3 8 1	3 7 1	3 6 9
2	1. 0	0. 2	3 8 4	3 7 3	3 7 2
3	1. 0	0. 2	3 8 9	3 7 8	3 7 8
4	1. 0	0. 2	3 8 4	3 7 4	3 7 3
5	1. 0	0. 2	3 8 8	3 7 6	3 7 5
6	1. 0	0. 2	3 8 0	3 6 7	3 6 5
7	1. 0	0. 2	3 8 2	3 7 2	3 7 4
A	1. 0	0. 2	4 0 2	3 9 3	3 9 1
B	1. 0	0. 2	3 9 5	3 8 6	3 8 4
C	1. 0	0. 2	4 1 1	4 1 8	4 1 6
D	1. 0	0. 2	4 0 5	3 9 6	3 9 3

As for the catalysts 1-7 of the example of this invention, from a table 4, 367 degrees C - 378 degrees C and 50% clarification temperature after durability of NO_x have [50% clarification temperature after durability of HC] 381 degrees C - 389 degrees C and 50% clarification temperature after durability of CO in the range which is 365 degrees C - 378 degrees C. On the other hand, as for catalyst A-D of the example of a comparison, 386 degrees C - 418 degrees C and 50% clarification temperature after durability of NO_x have [50% clarification temperature after durability of HC] 395 degrees C - 411 degrees C and 50% clarification temperature after durability of CO in the range which is 384 degrees C - 416 degrees C.

[0053] At catalyst A-D of the catalysts 1-7 of the example of this invention, and the example of a comparison, clarification temperature averages after [durability] 50%, by HC, 29 degrees of catalysts 1-7 of the example of this invention are by 13 degrees C and CO, and 28 degrees C and all are low by NO_x. That is, the catalysts 1-7 of the example of this invention have high endurance, and are understood that catalytic activity is maintained so much highly.

[0054]

[A table 5]

触媒	担持量 (g/l)		耐久後50%浄化温度 (℃)		
	P t	R h	H C	C O	N O _x
8	0. 3	0. 1	4 2 1	4 2 4	4 1 6
E	0. 3	0. 1	4 4 9	4 5 2	4 4 3
9	3. 0	0. 3	3 9 8	3 9 6	3 8 0
F	3. 0	0. 3	4 2 8	4 2 5	4 1 4
10	5. 0	0. 5	4 1 5	4 0 8	4 0 6
G	5. 0	0. 5	4 3 6	4 2 2	4 2 3

The catalyst 8, the catalyst 9, and catalyst 10 of an example of this invention have low 50% clarification temperature after durability like [the result of a table 5] the result of a table 4 as compared with Catalyst E, Catalyst F, and Catalyst G of the example of a comparison. That is, it turns out that the catalyst 8, the catalyst 9, and catalyst 10 of an example of this invention are all excellent in endurance ability.

[0055]

[A table 6]

触媒	担持量 (g/l)			耐久後50%浄化温度 ()		
	P t	P d	R h	H C	C O	N O _x
11	0. 5	0. 5	0. 2	4 1 5	4 0 8	4 0 6
H	0. 5	0. 5	0. 2	4 3 6	4 2 2	4 2 3
12	—	1. 0	0. 2	4 3 1	4 3 2	4 3 3
J	—	1. 0	0. 2	4 5 3	4 5 1	4 5 4

The catalyst 11 and catalyst 12 of an example of this invention have low 50% clarification temperature after durability like [the result of a table 6] the result of a table 4 and a table 5 as compared with Catalyst H, Catalyst F, and Catalyst J of the example of a comparison. That is, it turns out that the catalyst 11 and catalyst 12 of an example of this invention are all excellent in endurance ability.

(Example 2 of a trial) The palladium particle diameter after the durability of the catalyst of the platinum particle diameter after the durability of the catalyst of an example 1 and the example 1 of a comparison, an example 11, and the example 8 of a comparison was measured by XRD (X diffraction). A garden result is shown in the 7th table.

[0056]

[A table 7]

	P t 粒子径 (Å)		P d 粒子径 (Å)
触媒 1	9 8	触媒 1 1	2 0 5
触媒 A	2 0 2	触媒 H	3 1 7

The catalyst 1 for exhaust gas clarification and catalyst 11 of this invention have the diameter of a very fine particle of platinum and palladium smaller than the thing of the catalyst A of the example of a comparison, and Catalyst H from a table 7. Thereby, as for the catalyst 1 for exhaust gas clarification and catalyst 2 of this invention, it turns out that sintering of platinum and palladium is controlled.

[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The cycle diagram showing the engine drive of the aging (aging) trial made to each catalyst of the example of this invention, and the example of a comparison.

[Translation done.]